REACTIONS OF ACTIVE METHYLENE COMPOUNDS WITH QUINOLINIUM SALTS

BY

ROBERT LINCOLN FOSTER

B.S., Monmouth College, 1948
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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REACTIONS OF ACTIVE METHYLENE COMPOUNDS WITH QUINOLINIUM SALTS

Introduction

The patent literature (1) describing the reaction of quinolinium salts with nitromethane, phenylacetonitrile and acetoacetic ester proposed a 2-substituted 1,2-dihydroquinoline structure for the products obtained. The reaction product from 1-methylquinolinium iodide and nitromethane has recently been identified as 1-methyl-4-nitromethylenequinolane (2).

The structure of 1-methyl-4-nitromethylenequinolane was established by reduction of its monohydrobromide to an amine which was found to be identical with that obtained by reduction of 1-methyl-4-cyanoquinolinium iodide. The reaction of nitromethane with 1,2-dimethylquinolinium iodide produced 1,2-dimethyl-4-nitromethylenequinolane, but no product was obtained from 1,4-dimethylquinolinium iodide.

Discussion Of Results

The product of the reaction between phenylacetonitrile and 1-methylquinolinium iodide in the presence of base has been shown to be 1-methyl-4-(α-cyanobenzyl)-1,4-dihydroquinoline. The position of the substituent was established by conversion of the nitrile to an amide and reduction in two stages to the corresponding decahydroquinoline. This decahydroquinoline was compared with the reduction product of 1-methyl-4-(α-carbamylbenzyl)-quinolinium chloride which was prepared by an unequivical synthesis. The two amines were identical. The position of the double bond was shown by comparison of the ultraviolet spectrum with spectra of other 1,4-dihydroquinolines.

α-Phenylpropionitrile reacts with 1-methylquinolinium iodide yielding 1-methyl-4-(α-cyano-α-methylbenzyl)-1,4-di-

hydroquinoline. The structure of this compound was established by its identity with the product of methylation of 1-methyl-4-(α-cyanobenzyl)-1,4-dihydroquinoline.

The preparation and properties of 1-methyl-4-(α-cyano-*p*-methylbenzyl)-1,4-dihydroquinoline and 1-methyl-4-(α-cyano-*o*-methylbenzyl)-1,4-dihydroquinoline have also been described.

Malononitrile reacted with 1-methylquinolinium iodide to produce 1-methyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline. 1-Methyl-4-chloroquinolinium iodide reacted with malononitrile to give an identical compound, thus establishing the structure. Malononitrile and 1,2-dimethylquinolinium iodide gave 1,2-dimethyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline.

The condensation-dehydrogenation reaction observed with nitromethane and malononitrile also occurs with ethyl cyanoacetate. Ethyl cyanoacetate reacted with 1-methyl- and 1,2-dimethyl-quinolinium iodide to give 1-methyl- and 1,2-dimethyl-4-(α-carbethoxy-α-cyanomethylene)-1,4-dihydroquinoline, respectively.

Anomalous results were obtained with nitroethane, 1-nitropropane, 2-nitropropane and ethyl 2-pyridylacetate. No product was obtained from 1-methylquinolinium iodide and acetonitrile, ethyl phenylacetate, malonic ester or acetoacetic ester.

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VITA

The author was born on September 10, 1924, in Monmouth, Illinois. After graduation from Monmouth High School in 1942, he entered Monmouth College. From 1943 to 1946 he served in the Army of the United States. Following discharge from the Army he returned to Monmouth College and received a Bachelor of Science degree in 1948. He entered the Graduate College of the University of Illinois in September, 1948, and received the degree of Master of Science in June, 1949.